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Potential Use of Low-Cost Agri-Food Waste as Biosorbents for the Removal of Cd(II), Co(II), Ni(II) and Pb(II) from Aqueous Solutions

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Abstract: We evaluated the potential use of agri-food waste for the removal of heavy metal ions from aqueous solutions and its application in different processes (e.g., water remediation, in the production of biomass enriched in nutritionally significant elements, etc.). Biomasses from grape seed, grape pomace, loquat seed, Calabrese broccoli stem, empty pods of carob and broad bean pods, unripe bitter orange peel, kumquat, orange pulp and Canary Island banana pulp were prepared. The percentages and biosorption capacities were evaluated and compared with those refe-renced using Valencia orange peel (*Citrus sinensis* Valencia late). These studies allow for easily providing added value to different agri-food wastes. The results show that the proposed biomasses were able to retain the studied metal ions and obtained different percentages, being in some cases above 90%. The highest values were obtained using broad bean pod (Pb(II) (91.5%), Cd(II) (61.7%), Co(II) (40.7%) and Ni(II) (39.7%)). Similar values were observed using grape seed, broccoli stem, carob pod and unripe bitter orange peel. Carob pod for biosorption of Cd(II) is also of great interest. These studies suggest that the agri-food residues evaluated can be applied to prepare effective biosorbents of divalent metal ions from aqueous solutions.

Keywords: biomass; revaluation of agri-food waste; heavy metals; biosorption; water remediation

1. Introduction

In recent years, there has been a special interest in finding applications and methodologies to give value to agri-food wastes. As they are waste substances with little interest in the market, the cost of their use in any field will be low. In general, the characteristics of agri-food wastes are numerous and depend on the raw material and their generation process; however, they all share a main characteristic, which is their high content of organic matter [1]. Cellulose, hemicellulose and lignin are among their main constituents, although in different proportions [2], presenting hydroxyl, carbonyl and carboxyl groups as the main functional groups [3,4]. The research studies about waste reuse are interesting and some are financed by projects such as Agrowaste (LIFE10 ENV/ES/469) [5] or Agrocycle. The latter was carried out in the past five years within the framework of the European "Horizon 2020" projects in cooperation with the People's Republic of China, addressing the recycling and valorization of agri-food industry wastes [6].

On the other hand, the treatment of industrial effluents is a laborious process due to the wide variability of substances that the wastewaters might contain (organic or inorganic components, extreme acid or basic substances, volatile compounds, etc.). At the same time, these treatment processes must be compatible with the needs and economic viability of the industry, which is to cover the treatment in most cases. The main pollutants can be classified as those of organic origin, such as hydrocarbons and pesticides, and those of inorganic character, such as heavy metals, characterized by density higher than 5 g·cm^{-3} [7–9].

Nowadays, the most common methods to remove these elements from wastewaters are chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and sorption techniques [10,11]. Some of these techniques can be expensive due to the high operational costs and energy requirements. Thus, small industries do not have access to these processes and generally choose to discharge their waters into common septic tanks or even deep wells [12]. Methodologies that use low-cost materials such as agri-food wastes are alternative solutions to the problem. It is also worth mentioning the use of enrichment of biomass in nutritionally significant elements as their carrier in feeding animals and nutrition of plants [13].

Sorption techniques are considered among the best options in pollutant removal due to their simplicity and efficiency [14]. Activated carbon is a widely used sorbent that has proven to be useful in the removal of heavy metals and other contaminants from aqueous solutions [15–19]. However, its application in wastewater treatments is not feasible due to its high cost associated with the need for regeneration [20]. Because of this, the latest advances and studies have focused on the search for new efficient and low-cost alternatives for the removal of heavy metals using other substances [10,21–23].

Agri-food waste can be a suitable alternative, with a high sorbent capacity mainly due to the presence of hydroxyl and carboxyl groups. These types of residues that are composed of biological material are considered biosorbents.

Thus, the novelty of this study is that we identify new, inexpensive inert biosorbents from abundant and available agri-food waste for use in heavy metal remediation processes or other purposes, providing, at the same time, an added value to this waste.

Due to the potential of agri-food wastes as biosorbents, we studied the removal of heavy metals by different types of biomass. They were prepared from grape seed (*Vitis vinifera* Palomino Fino), grape pomace (*Vitis vinifera* Cabernet Sauvignon), loquat seed (*Eryobotria japonica*), Calabrese broccoli stem (*Brassica oleracea* Italica), empty pods of carob (*Ceratonia siliqua*) and broad bean (*Vicia faba*), unripe bitter orange peel (*Citrus aurantium*), kumquat (*Citrus japonica*), orange pulp (*Citrus sinensis* Valencia late) and Canary Island banana pulp (*Musa acuminata* Colla (AAA)) in order to evaluate their sorption capacities in the removal of divalent metal ions from an aqueous medium. A biosorbent prepared from orange peel (*Citrus sinensis* Valencia late) was used as a reference biomass. The first two biosorbents mentioned above were selected because of the economic benefit of using wine industry wastes, especially in areas with long winemaking traditions. The loquat is a seasonal consumption fruit tree; however, its ornamental use is also widespread. Its seed occupies a large percentage of the fruit, not having nutritional properties. Broccoli stem and empty carob and broad bean pods are by-products already in use in the processing of flour, frozen products and pre-cooked meals. Bitter orange peel and kumquat can be alternative biosorbents to the common orange, since their main use is ornamental. Although fruit pulps of common orange and banana are not waste products, they can become so in the case of fruits past their expiration dates, surplus or after obtaining juices or concentrates.

Laboratory-scale experiments were carried out with the selected biomasses, and their potential capacities as heavy metal biosorbents were evaluated and compared to the results obtained with Valencia late orange peel in the same conditions as described in the literature. This is an efficient agri-food waste that is easy to obtain and is generated in large quantities by juice manufacturing industries. Its efficient biosorption capacity is due to its pectin content that easily retains metal ions. For this reason, it has already been used successfully by other authors for heavy metal biosorption [11,24,25]. Therefore, it is used as a reference in this study.

The biosorption tests were carried out for Cd(II), Co(II), Ni(II) and Pb(II) ions, which are of significant toxicological and environmental interest. Cadmium and lead are non-essential elements without biological function and are toxic at any concentration. Cobalt is part of vitamin B12, but high levels of this element may be harmful; this is also true for nickel. In fact, the International Agency for Research on Cancer [26] classifies cadmium and nickel compounds as carcinogenic to humans (Group 1), lead inorganic compounds as probable

carcinogens (Group 2A) and cobalt soluble salts and other compounds of cobalt as possible carcinogens (Group 2B), hence the interest in their removal from industrial effluents. The proposed tests were performed using the biosorbents prepared from the selected wastes after their pretreatment. The biosorbents and metal solutions were in contact for 24 h, allowing us to evaluate the efficiency of the biosorption process by analyzing the solutions by atomic absorption spectroscopy (AAS).

2. Materials and Methods

2.1. Cleaning Protocol

As this research was based on the analysis of trace metal concentrations, a cleaning protocol was necessary to avoid contamination of solutions and samples. Double gloving (of nitrile and non-colored plastic polyethylene) was used when handling the materials. The cleaning protocol followed these steps: (a) pre-clean with water and soap; (b) rinse with Milli-RO water; (c) rinse with 2 mol L^{-1} HNO_3 (PRS-CODEX 69%, Panreac, Barcelona, Spain) solution; (d) three consecutive rinses with Milli-RO or Milli-Q water, depending on the samples concentrations. Finally, the clean material was allowed to dry inside a laminar flow hood cabinet (Captair Cruma 870 FL, Barcelona, Spain).

2.2. Reagents and Solutions

The sorption processes were carried out using the following salts as metal ion precursors: $Cd(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Pb(NO_3)_2$ (pro-analysis, Panreac, Barcelona, Spain). The pH values of aqueous solutions were adjusted with an acetic acid/acetate buffer solution, prepared with acetic acid CH_3COOH (pro-analysis 96%, Merck, Darmstadt, Germany) and NaOH (pro-analysis 98%, Panreac, Barcelona, Spain). To avoid metal ion precipitation over time, the aqueous solutions were prepared at the time of use. Water was purified by reverse osmosis (Milli-RO) with an Elix 3 system followed by ion exchange with an 18.2 MΩ cm (25 °C) Milli-Q^{50} deionized water system (Millipore, Burlington, MA, USA).

2.3. Preparation of the Biosorbents

Each raw material was collected in different periods of the year. Then, the different portions were treated as described below and mixed altogether to ensure the homogeneity of samples and the repeatability of results. Thus, the different biosorbents were prepared from selected agri-food waste, following a first pretreatment that consisted of (a) washing with deionized water, (b) cutting into small pieces and (c) drying in an oven at different temperatures (Table 1) until constant weight, avoiding high temperatures so as not to degrade the organic components of the biomass. The selected temperature values were conditioned by the moisture content of the sample and they were selected in order to avoid the generation of fungi in the samples. The pretreatment was slightly different for the Palomino Fino grape seeds and the Cabernet Sauvignon grape pomace, which were co-llected as residue from the vinification process, then washed with deionized water, dried in a temperature-controlled chamber and cryogenically grinded.

After the drying, biomasses were crushed, ground in an agate mortar and sieved. To facilitate the sieving, a first stage was carried out with a 60 mesh size sieve (0.246 mm), and then the biomass was sieved using a 120 mesh size sieve (0.125 mm) (stain-less steel sieve, CISA, Barcelona, Spain). Only the last fraction with the smallest particle size was used in further studies.

To carry out the biosorption tests, two aqueous solutions were prepared: (a) solution 1: 1 mmol L^{-1} metal ion solution buffered at pH 4.8 with 0.1 mol L^{-1} CH_3COOH/CH_3COONa; (b) solution 2: blank solution buffered at pH 4.8 with 0.1 mol L^{-1} CH_3COOH/CH_3COONa. The metal ion concentrations measured in blank solutions were less than 0.5% with respect to those found in solution 1 after the biosorption process.

Table 1. Drying temperature values for the different biosorbents.

Biosorbent	Drying Temperature (°C) [1]
Palomino Fino grape seed (*Vitis vinifera* Palomino Fino)	40
Cabernet Sauvignon grape pomace (*Vitis vinifera* C. Sauvignon)	42
Loquat seed (*Eryobotria japonica*)	60
Calabrese broccoli stem (*Brassica oleracea* Italica)	45
Empty carob pod (*Ceratonia siliqua*)	60
Empty broad bean pod (*Vicia faba*)	40
Unripe bitter orange peel (*Citrus aurantium*)	45
Kumquat (*Citrus japonica*)	40
Valencia late orange pulp (*Citrus sinensis* Valencia late)	120
Canary Island banana pulp (*Musa acuminata* Colla (AAA))	120 (2 h) + 40
Valencia late orange peel (*Citrus sinensis* Valencia late)	40

[1] Drying until constant weight.

The pH of the solution is one of the parameters to take into account. Low values of pH (pH < 3) can cause the competition of H^+ ions for active sites on the surface of the biomass. At higher pH values, the acid functional groups from the biomass are deprotonated and the competitive effect of hydrogen ions diminishes. In addition, the sorption of positive ions such as Cd(II), Co(II), Ni(II) or Pb(II) can be supported if the surface charge is negative. However, high values of pH can lead to the hydrolysis and precipitation of metal ions in their hydroxide forms [25,27]. For this reason, the usual range of preliminary biomass studies is a pH of 3–6 [28]. Thus, an intermediate pH value of 4.8 was selected that also avoided producing acid waste solutions where possible during these studies, in accordance with the green analytical chemistry principles. Other papers reported studies with similar pH values [25,29–40].

The metal ion concentrations were analyzed in the aqueous solutions after the biosorption process. For that, according to the equipment sensitivity specifications and the optimal instrumental conditions of the atomic spectroscopy spectrometer (iCE 3000 Series Atomic Absorption (AA), Thermo Scientific, Waltham, MA, USA), calibration curves were prepared.

2.4. Batch Biosorption Studies

Four experiments were carried out for each biosorbent and metal ion solution. Single-component metal ion solutions were used in these studies. Batch experiments were performed in 100 mL polypropylene containers (Deltalab, Barcelona, Spain). Two replicated experiments were performed by adding 50 mL of solution 1 to 0.5 g of biosorbent. The third experiment was carried out as a control test with 50 mL of solution 2 and 0.5 g of biosorbent. Finally, to evaluate the real concentration of metal ions in solution 1, a fourth experiment was performed with 50 mL of solution 1 in the absence of biosorbent in order to evaluate the initial metal concentration to which the biosorbent was exposed during the experiments.

The suspensions were stirred using an orbital laboratory shaker (IKA HS501D Labortechnik, Wasserburg am Bodensee, Germany) at 200 rpm for 24 h at 23 °C. After the extraction process, the resulting mixtures were vacuum-filtered on a 47 mm standard Millipore filtration assembly (MerckMillipore, Darmstadt, Germany) with 0.5 μm Whatman® glass microfiber filters (Whatman, Maidstone, UK)) connected to a D95 model DINKO vacuum pump (Dinko Instruments, Barcelona, Spain).

The removal of metal ions by biosorption (in percentage) for each biosorbent was determined as follows:

$$\text{Biosorption (\%)} = \frac{C_0 - C_t}{C_0} \cdot 100 \tag{1}$$

where C_o and C_t are the initial and t-time concentrations of metal (mg L^{-1}) in the aqueous solution, respectively. With this percentage, the biosorption process efficiency was evaluated for each metal ion and biosorbent studied. In addition, the biosorption capacity Q_t (expressed in mg g^{-1}), defined as the amount of metal ions sorbed per unit weight of biosorbent, was also calculated from the following equation:

$$Q_t = \frac{V \cdot (C_0 - C_t)}{W} \tag{2}$$

where V is the volume of the solution (L) and *m* is the mass of the biosorbent (g).

There are several studies on metal ion removal that use the biosorption capacity parameter [41,42], which is a complementary parameter to the sorption percentage value. Nevertheless, this parameter is not appropriate to compare different metal ions with different atomic weights, since the parameter is expressed in mg g^{-1} instead of mmol g^{-1}. Thus, it is necessary to normalize this parameter and express it as mmol g^{-1} ($Q_t{}'$).

3. Results and Discussion

Table 2 shows the biosorption percentages of Cd(II), Co(II), Ni(II) and Pb(II) in aqueous solution for different biosorbents, showing Pb(II) with the highest biosorption percentage for all the biosorbents studied. For this metal, the cation retention capacity was higher for the empty broad bean pod (91.5%) and the Palomino Fino grape seed (89%) than for the Valencia late orange peel (88.2%), which was used as a reference biosorbent (these studies were carried out under the same experimental conditions). A percentage of 83% was obtained using the empty carob pod, similar to the percentage for orange peel, but slightly lower. Thus, these three biosorbents can be applied with the same or higher efficiency than the Valencia late orange peel for the bioremediation of water contaminated with Pb(II).

By comparing the results of the other three metals, the best values were obtained for Cd(II) biosorption for all the biosorbents, with the exception of grape pomace, which presented a sorption percentage of 11.2% for Ni(II), a little higher than the percentage of 8.1% for Cd(II) and 7.1% for Co(II); however, these percentages do not have significant differences among them and the values are low, resulting in biosorbents with little potential for removal. While sorption percentage values of Cd(II) were lower than those obtained for Pb(II), when using empty carob pod (61%) and empty broad bean pod (61.7%), similar values of Cd(II) biosorption were obtained compared with the reference biosorbent Valencia late orange peel (65.2%), although slightly lower.

Furthermore, the biosorption percentages for Co(II) and Ni(II) with empty broad bean pod were near to but slightly lower than those obtained with orange peel (40.7% vs. 47.9% and 39.7% vs. 49%, respectively).

On the other hand, it was possible to compare the results obtained in the present work with those found in the scientific literature for the sorption of these same metal ions with different biosorbents, which are summarized in Table 3. As it can be observed in Table 3, some biosorbents were modified by means of a carbonization process, a chemical modification (with NaOH, Ca(OH)$_2$, HNO$_3$, citric acid, TiO$_2$ ...) or using nanoparticles, among other methods. The orange peel used in this work as a reference biosorbent has been used by different researchers with modifications or chemical treatments, obtaining

satisfactory results (higher than 90%). However, it requires biosorbent pretreatments that can complicate and make biomass preparation more expensive. In this work, the values obtained for Pb(II) using the empty broad bean pod (91.5%) or the Palomino Fino grape seed (89%) were similar to those found in the literature, and present the advantage of their direct use. For the other metal ions studied, similar pretreatments to those described for the biomasses in Table 3 could be applied in order to try to improve the results.

Table 2. Biosorption percentage of Cd(II), Co(II), Ni(II) and Pb(II) in aqueous solution for the different biosorbents studied.

Biosorbent	Biosorption (%) [1]			
	Cd(II)	Co(II)	Ni(II)	Pb(II)
Palomino Fino grape seed (*Vitis vinifera* Palomino Fino)	30.1	18.5	13.4	89.0
Cabernet Sauvignon grape pomace (*Vitis vinifera* C. Sauvignon)	8.1	7.1	11.2	66.0
Loquat seed (*Eryobotria japonica*)	28.5	15.0	13.7	36.6
Calabrese broccoli stem (*Brassica oleracea* Italica)	48.9	28.4	24.8	78.1
Empty carob pod (*Ceratonia siliqua*)	61.0	20.8	22.1	83.0
Empty broad bean pod (*Vicia faba*)	61.7	40.7	39.7	91.5
Unripe bitter orange peel (*Citrus aurantium*)	37.3	30.5	25.5	65.5
Kumquat (*Citrus japonica*)	29.2	9.1	8.7	32.8
Valencia late orange pulp (*Citrus sinensis* Valencia late)	47.6	31.5	28.9	75.4
Canary Island banana pulp (*Musa acuminata* Colla (AAA))	41.7	4.7	11.5	70.4
Valencia late orange peel (*Citrus sinensis* Valencia late)	65.2	47.9	49.0	88.2

[1] Conditions: metal ion concentration: 1 mmol L^{-1}; particle size: <0.125 mm; contact time: 24 h; amount of biosorbent: 10 g L^{-1} biosorbent in metal solution.

The sorption capacity values expressed in mg g^{-1} (Q_t) and mmol g^{-1} (Q_t') were calculated from the experimental results (Table 4). The Q_t' values show that the best results were obtained for Pb(II), with sorption capacity values higher than 0.06 mmol g^{-1} for all the biosorbents studied, with the exception of loquat seed and kumquat biomasses.

Comparing these values with those obtained for the reference biomass (0.095 mmol g^{-1} for Pb(II) with Valencia late orange peel), it can be concluded that most of these biomasses can be potentially useful to retain this metal ion. As indicated, for the rest of the metal ions, the sorption capacities were lower than for Pb(II). Nevertheless, there was an exception when empty broad bean pod was used as a biosorbent, showing a slightly higher value for Cd(II) (0.079 mmol g^{-1}) than for Pb(II) (0.075 mmol g^{-1}). This and some of the other biosorbents studied exceeded the value obtained for Cd(II) for the reference biosorbent (0.028 mmol g^{-1}): Palomino Fino grape seed (0.030 mmol g^{-1}), empty carob pod (0.061 mmol g^{-1}) and unripe bitter orange peel (0.037 mmol·g^{-1}). Similar values were also obtained with broccoli stem (0.028 mmol g^{-1}) and kumquat (0.029 mmol g^{-1}) biomasses.

Table 3. Literature review of biosorption percentages of Cd(II), Co(II), Ni(II) and Pb(II) using di-fferent biosorbents.

Metal	Biosorbent	Biosorption (%)	Reference
Cd(II)	Unmodified/modified oil palm bagasse with Al_2O_3 nanoparticles	87%/91.2%	[43]
	Curry leaf powder	68.5%	[44]
	Charred orange peel	99%	[24]
	Cucumber peel	84.8%	[29]
	Chemically modified orange peel	81.0%	[25]
	Rice straw	80%	[45]
	Modified orange peel with NaOH and $CaCl_2$	93.6%	[46]
	Banana peel	89.2%	[47]
Co(II)	Tamarind peel	6.8%	[48]
Ni(II)	Unmodified/Modified oil palm bagasse with Al_2O_3 nanoparticles	81%/86.9%	[43]
	Modified sweet potato peel with TiO_2	86.7%	[49]
	Modified cassava peel with TiO_2	81.5%	[49]
	Peat	92.5%	[30]
	Modified orange peel with NaOH and $CaCl_2$	92.2%	[46]
	Cashew nut shell	77.7%	[31]
	Pomegranate peel	78%	[50]
Pb(II)	Curry leaf powder	84.7%	[44]
	Peat	100%	[30]
	Modified sweet potato peel with TiO_2	99.8%	[49]
	Modified cassava peel with TiO_2	99.8%	[49]
	Rapeseed	94.5%	[32]
	Cucumber peel	96%	[33]
	Malt bagasse	97.7%	[34]
	Peanut shell	85%	[35]
	Lentil husk	98%	[36]
	Native garlic peel	90%	[51]
	Mercerized garlic peel with NaOH	97%	[37]
	Modified muskmelon peel with $Ca(OH)_2$	100%	[38]
	Cross-linking orange peel with $CaCl_2$	99.5%	[39]
	Chemically modified orange peel	99.5%	[25]
	Modified coffee waste with citric acid 0.6 M	70%	[51]
	Banana peel	85.3%	[47]
	Pine cone power	99.9%	[40]
	Unmodified/Modified Macadamia-derived activated carbon	74.7%/87.4%	[52]
	Corn cob activated carbon	77.5%	[53]
	Modified/Unmodified corn stalk biochar	78.8%/83.8%	[54]
	Modified/Unmodified rice stalk biochar	91.20%	[55]
	Acid-activated seagrass Posidonia oceanica	>95%	[56]

Table 4. Biosorption capacity Q_t (mg g^{-1}) and normalized biosorption capacity Q_t' (mmol g^{-1}) for Cd(II), Co(II), Ni(II) and Pb(II) of the biosorbents studied.

Biosorbent	Cd(II) [1]		Co(II) [1]		Ni(II) [1]		Pb(II) [1]	
	Q_t	Q_t' ($\times 10^2$)	Q_t	Q_t' ($\times 10^2$)	Q_t	Q_t' ($\times 10^2$)	Q_t	Q_t' ($\times 10^2$)
Grape seed	3.39	3.01	1.16	1.97	0.79	1.34	17.38	8.39
Grape pomace	0.34	0.30	0.28	0.48	0.54	0.91	15.12	7.30
Loquat seed	1.91	1.70	0.87	1.47	0.71	1.21	6.65	3.21
Broccoli stem	3.19	2.83	1.48	2.52	1.31	2.23	14.17	6.84
Empty carob pod	6.89	6.13	1.22	2.07	1.17	1.99	15.10	7.29
Empty broad bean pod	8.92	7.93	2.33	3.95	2.09	3.56	15.62	7.54
Unripe bitter Orange peel	4.15	3.69	1.99	3.38	1.66	2.82	12.48	6.02
Kumquat	3.21	2.86	0.55	0.94	0.58	0.99	5.91	2.85
Orange pulp	2.32	2.07	1.64	2.78	1.39	2.37	16.75	8.09
Banana pulp	1.76	1.56	0.13	0.23	0.55	0.93	15.97	7.71
Orange peel	3.14	2.80	2.50	4.24	2.36	4.03	19.60	9.46

[1] Conditions: metal ion concentration: 1 mmol L^{-1}; particle size: <0.125 mm; contact time: 24 h; amount of biosorbent: 10 g L^{-1} biosorbent in metal solution.

In the case of Co(II) and Ni(II) biosorption, the normalized sorption values for the empty broad bean pod biomass were comparable to the values obtained for the reference biosorbent (0.040 vs. 0.042 mmol g^{-1} for Co(II) and 0.036 vs. 0.040 mmol g^{-1} for Ni(II), res-pectively).

As a result, it can be stated that the empty broad bean pod is a viable low-cost alternative for the removal of Cd(II), Co(II), Ni(II) and Pb(II) from water, offering satisfactory results of normalized sorption capacity, even without optimizing the biosorption process. Likewise, some of the other studied biomasses, such as the empty carob pod, the Palomino Fino grape seed, the broccoli stem and the unripe bitter orange peel, are also interesting alternatives for future studies.

The Pearson correlation matrices were obtained with the normalized sorption capacity values to study the covariation grade (joint variation of variables) by comparing both the metal ions and the biomasses among them (Tables 5 and 6, respectively).

Table 5. Pearson correlation coefficients matrix [1] for normalized sorption capacity (Q_t') of Cd(II), Co(II), Ni(II) and Pb(II) among the studied metal ions.

Metal	Cd(II)	Co(II)	Ni(II)	Pb(II)
Cd(II)	1.000			
Co(II)	0.576	1.000		
Ni(II)	0.557	**0.966**	1.000	
Pb(II)	0.124	0.401	0.477	1.000

[1] High positive correlation: coefficient between 0.9 and 0.99 (highlighted in bold).

In these tables, the variables that correlated very highly—that is, with Pearson co-efficients between 0.9 and 0.99—are marked in red. Based on these results, it could be esta-blished that Co(II) and Ni(II) correlated very significantly with each other, with compa-rable variations (Table 5). Furthermore, the biomasses could be grouped into two typologies (Table 6): Group I (kumquat and empty broad bean and carob pods) (Figure 1) and Group II (Palomino Fino grape seed, Cabernet Sauvignon grape pomace, loquat seed, broccoli stem, unripe bitter orange peel, Valencia late orange pulp, Canary Island banana pulp

and Valencia late orange peel) (Figure 2), showing different trends if the sorption capacity va-lues for the four metal ions studied are compared.

Table 6. Pearson correlation coefficients matrix [1] for normalized sorption capacity (Q_t') of Cd(II), Co(II), Ni(II) and Pb(II) among the studied biomasses.

Biosorbent	Grape Seed	Grape Pomace	Loquat Seed	Broccoli Stem	Empty Carob Pod	Empty Broad Bean Pod	Unripe Bitter Orange Peel	Kumquat	Orange Pulp	Banana Pulp	Orange Peel
Grape seed	1.000										
Grape pomace	**0.959**	1.000									
Loquat seed	**0.999**	**0.955**	1.000								
Broccoli stem	**0.995**	**0.982**	**0.994**	1.000							
Empty carob pod	0.834	0.668	0.826	0.775	1.000						
Empty broad bean pod	0.681	0.466	0.675	0.603	**0.969**	1.000					
Unripe bitter orange peel	**0.997**	**0.945**	**0.999**	**0.989**	0.827	0.681	1.000				
Kumquat	0.722	0.528	0.712	0.650	**0.984**	**0.994**	0.714	1.000			
Orange pulp	**0.960**	**0.993**	**0.961**	**0.983**	0.648	0.449	**0.955**	0.502	1.000		
Banana pulp	**0.985**	**0.982**	**0.978**	**0.990**	0.794	0.620	**0.968**	0.678	**0.966**	1.000	
Orange peel	**0.914**	**0.984**	**0.915**	**0.951**	0.543	0.327	**0.907**	0.386	**0.991**	**0.933**	1.000

[1] High positive correlation: coefficient between 0.9 and 0.99 (highlighted in bold).
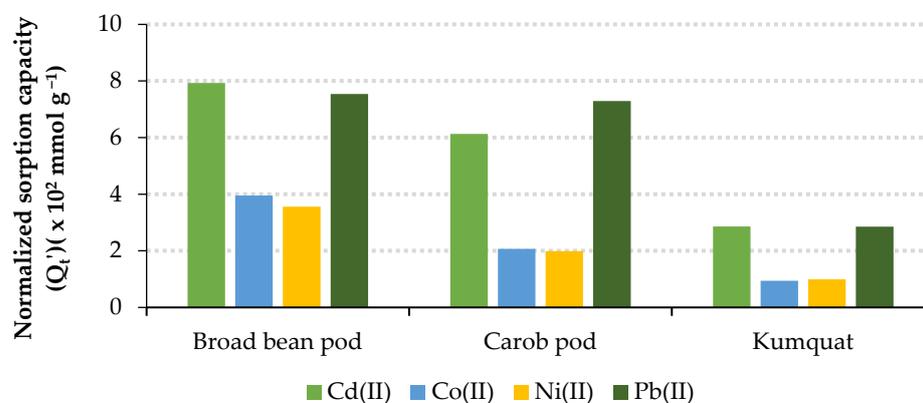
Figure 1. Normalized sorption capacity Q_t' (mmol g^{-1}) of metal ions for biomasses with high and positive correlation: Group I.

Table 5 shows that the sorption capacity values of Co(II) and Ni(II) correlated in a high and positive way (0.966); that is, they showed an outstanding trend or linear regression relationship with each other for the biomasses studied. Both elements presented similar behavior, with values always lower than those obtained for Pb(II) (Figures 1 and 2), an element for which no significant Pearson correlation was found with another ion. Regarding Cd(II), a high correlation coefficient with respect to the rest of the metal ions was not observed, with Q_t' values always higher than those for Co(II) and Ni(II) for the Group I biomasses and without any similar behavior for the Group II biomasses, being sometimes higher (for grape seed and banana pulp), similar (for loquat seed, broccoli stem and unripe bitter orange peel) or lower (for grape pomace, orange pulp and the reference biosorbent Valencia Late orange peel). Comparing Cd(II) with Pb(II), the Q_t' values for biomasses of Group I were similar, while for Group II biomasses, Cd(II) Q_t' values were lower than for Pb(II). Therefore, it is concluded that the Group I biomasses offer a similar potential for

the biosorption of Cd(II) and Pb(II), higher than that of Ni(II) and Co(II), while Group II biomasses have a greater biosorption potential for Pb(II), the behavior being va-riable for the other metal ions.
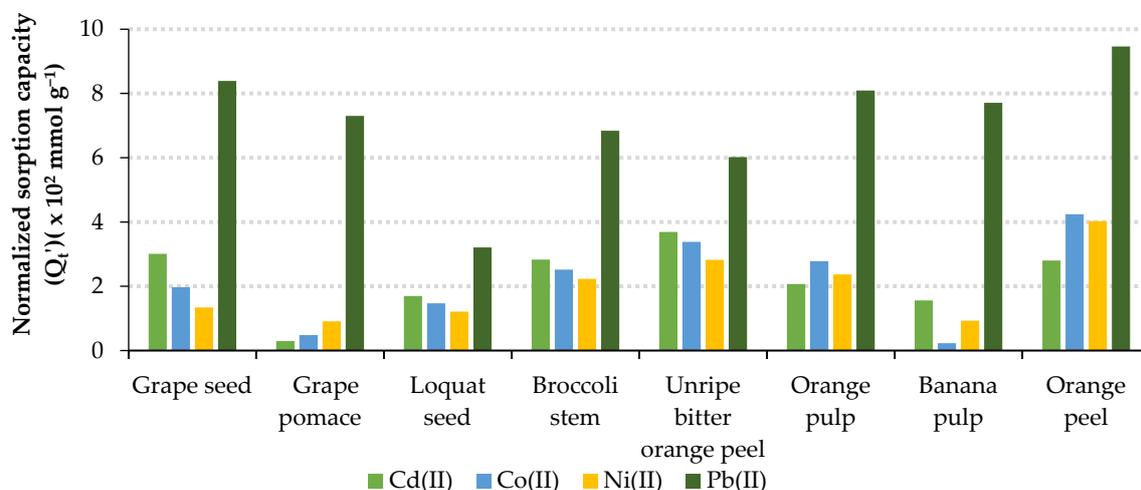
Figure 2. Normalized sorption capacity Q_t' (mmol g^{-1}) of metal ions for biomasses with high and positive correlation: Group II.

4. Conclusions

In this work, different biomasses from agri-food waste (grape seed, grape pomace, loquat seed, Calabrese broccoli stem, empty pods of carob and broad bean pods, unripe bitter orange peel, kumquat, orange pulp and Canary Island banana pulp) were prepared as biosorbents for the removal of divalent metals, such as Cd(II), Co(II), Ni(II) and Pb(II) ions, from aqueous solutions, and we investigated their potential application in separation processes.

The proposed biomasses were able to retain the studied metal ions, obtaining different percentages, being in some cases above 90%. It can be concluded that broad bean pod biomass is a potential alternative for the removal of these metal ions, providing efficient sorption capacity results (Pb(II) (91.5%), Cd(II) (61.7%), Co(II) (40.7%) and Ni(II) (39.7%)), even without optimizing the separation process. Some of the other biomasses studied, such as Palomino Fino grape seed, broccoli stem, carob pod and unripe bitter orange peel, are also interesting alternatives for further studies. The satisfactory results for Pb(II) biosorption with most of the biomasses studied stand out, with similar results to those obtained with Valencia late orange peel. The results obtained using empty broad bean or carob pod for the biosorption of Cd(II) are also of great interest, with much better biosorption capacity values than those obtained with the reference biomass.

From the comparative study of the metal ions, the high similarity between the biosorption of Ni(II) and Co(II) is noteworthy. In addition, the correlation of the sorption capacities among the studied biomasses allowed us to classify them into two groups: Group I, with a similar potential for the biosorption of Cd(II) and Pb(II), higher than that of Ni(II) and Co(II), and Group II, with a greater potential for the Pb(II) biosorption, the behavior being variable for the rest of the metal ions, but always lower.

These findings suggest that the biosorbents prepared from agri-food waste can be applied in the sorption of divalent metal ions for the removal of heavy metal ions from aqueous solutions, with applications in different processes such as water remediation or other purposes.

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tion, validation. M.D.G.-R.: Conceptualization, methodology, investigation, writing—original draft, writing—review and editing, supervision, resources, funding acquisition. M.D.G.-C.: Conceptualization, methodology, investigation, validation, writing—original draft, writing—review and editing, supervision. All authors have read and agreed to the published version of the manuscript.

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